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(71) Applicants
Hubert von Blücher,
Sohnstrasse 56, 4000
Düsseldorf, Germany
Hasso von Blücher,
Sohnstrasse 56, 4000
Düsseldorf, Germany
(72) Inventors
Hubert von Blücher
Hasso von Blücher
(74) Agents
Eric Potter & Clarkson,
14 Oxford Street,
Nottingham NG1 5BP

(54) **Adsorbent material**

(57) A material for protection against chemicals and short-term heating effects is made up of an air-permeable flexible base or support layer for adsorber particles, more specially, porous ones, which are placed on support columns or hairs on at least one side of the support layer.

In a process for making the material, the adhesive composition is put on to the base or support material at separate points or dots in a viscous form and then the adsorber grains are placed on top of the composition. Then, by the action of centrifugal force or otherwise, the adsorber grains are moved upwards, away from the support layer, pulling out hairs or columns of the adhesive composition, which are then changed into a solid condition.

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SPECIFICATION

A material for protection against chemically damaging substances and short-term heating effects and a process for making it

The invention is with respect to a material for protection against chemically damaging substances and short-term heating effects, made up of an air-permeable flexible support layer for adsorber particles, more specially porous adsorber grains, and to a process for producing such a material.

For the designing and producing protection systems, more specially clothing for the protection of human beings and, however, furthermore in the case of medical apparatus, air-conditioning systems, water-treating systems and the aircraft industry, there is a need for flexible filter material able to keep back or keep out poisonous or otherwise damaging vapors and gases.

Such an effect is produced, for example, by the material of the German Offenlegungsschrift specification 2,400,827, which is made up of an open-pored, flexible foam material base and adsorber particles on the pore walls, in which respect the specially useful effect produced is that the material only has a relatively low resistance to gas currents.

If, however, in addition to damaging substances in the form of gases or vapors, liquid damaging or aggressive substances come into question, so far the only possible step has been that of using a heavy upstream or inlet filter unit for the absorption of liquid with a complete loss of the very markedly useful effects of a flat, sheet-like filter, as for example a low weight, flexibility, a low thermal insulation effect and a high ventilation effect.

More specially, in the case of protection systems used under rough conditions, as for example in the case of fires and other accidents in chemical plant, it has so far been necessary to make use of apparatus specially designed for the different damaging chemicals in question, which are most likely to come into question, in which respect for light-weight protective clothing, designed to make it possible for the user to go into a dense cloud of mist of damaging substance, it would only be able to make use of these very useful properties to a limited extent, because such material is hardly resistant at all to liquids in comparison with damaging gases.

For putting an end to these shortcomings, a suggestion has been made in the past for a material of the German Offenlegungsschrift specification 2,400,827, to be made with porous adsorber grains seated in the pores of the foam material. Such adsorber grains within the material hardly have any effect stopping the current of gas through the pores, while on the other hand, being porous, they have the property of taking up liquids and absorbing damaging materials, and, even after generally all the adsorber grains had taken up their full amount of liquid, the permeability to gas is not decreased to anything more than a small degree (see the German Offenlegungsschrift specification 2,804,154).

The material of the German Offenlegungsschrift

specification 2,804,154 not only makes possible the design of flexible air or gas filters, able to take up great amounts of liquid, but furthermore it is possible for the material to be used as a liquid filter, because, in view of the effect of the porous adsorber grains, the time that liquid elements are in the material is increased. Furthermore, this filter material is able to take up and keep within it great amounts of damaging liquid substance without the substance running right through the filter. If evaporation of the liquid damaging substance in the adsorber grain takes place, the vapors produced will be adsorbed by the adsorber particles seated on the pore walls.

However, there is a shortcoming with the system of the German Offenlegungsschrift specification 2,804,154, inasmuch as the flexible foam material base takes up a great amount of space, that is to say it has a generally high bulk. Furthermore the foam material base makes the old filter material less pliable.

For these reasons, one purpose of the present invention is that of designing a material of the sort named at the start which has a very much lower bulk or specific volume while keeping to the same weight and having better adsorption properties and a higher pliability.

A further purpose of the present invention is that of designing a process for producing such a material.

With respect to the product of the process, the purpose is effected in that the adsorber grains are seated on the support columns, present on at least one side of the support layer.

With respect to the process the purpose in question is effected in that, at separate points an adhesive composition, which at the start is viscous, is placed on the support layer, the adsorber grains are placed on the adhesive composition while still viscous and then this half-completed product is mechanically so processed that the adsorber grains have the effect of pulling up the adhesive composition to take the form of support columns and the adhesive composition is then changed into a solid form.

The material of the present invention is in the form of a light-weight filter material with a very low specific volume and with a surprisingly high adsorption capacity.

More specially, the support layer takes the form of a textile fabric, as for example cotton fabric, which is highly air-permeable, is resistant to boiling water and, if after-processed in the right way, is fire-proof. The structure of the material of the invention is to be such that, under a vacuum of 10 mm Hg the permeability is 1500 liter/m²s.

On the support layer, whose one side is made somewhat rough, firstly at separate points a more specially thermoplastic adhesive composition is placed, which at the start is viscous, and the adsorber grains are then run onto the composition, more specially by dropping them onto or otherwise putting them in contact with the face of the composition. Then the half-completed product is so processed that the adsorber grains have the effect of pulling the adhesive composition up as support columns, before the composition becomes a solid form.

In this way, it is possible to make certain that, for example, toxic substances in the vapor phase may get to nearly all sides of the adsorption grains. The filtering effect is greatly increased because of the structure of the material in the present invention.

- 5 The adsorber grains are made up of organic or inorganic starting materials and have spaces for taking up further substances (additives) such as heavy metal catalysts, fire-inhibitors, antibacterial and fungicidal substances.

- 10 In the thermoplastic adhesive composition it is furthermore possible for additives to be placed (this being in fact a preferred form of the invention) helping the adsorption tracts of the adsorbing substances in taking effect and stopping any migration and, for this reason, over-early aging of the synergetic system.

A preferred form of the adhesive composition may be:

- 20 polymer (in latex form) 100 parts
zinc oxide 5 parts
sulfur 1 part
carbon black 3 parts
hard kaolin 10 parts
25 thiocarbanilide 1 part
zinc dibutyldithiocarbamate 2 parts.

Furthermore, it is possible to make use of latices coming from different sources, such as chloroprenes, natural latices, acrylates, polyurethanes, silicone rubber, fluoroprenes, polyvinylidenes and compounds and/or mixtures of them.

- 30 Certain salts, that is to say:
3% $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (copper nitrate) on metal
1.5% of silver nitrate on metal

- 35 1% of nitrate on chromium
have turned out to be additives with a very high catalytic efficiency.

- The adhesive composition is best made up as a batch with a pot life of 12 hours. Such compositions are used up at once in the production process.

- 40 For stopping any flame development in the material when heated, after burning and smouldering, the adhesive composition may be made containing iron chloride (produced in the vapor phase) with a ratio of 45 1 to 30. The agglomeration of the heavy metal additives with the flame-proofing substances takes place at the time of polymerization of the adhesive aggregate without, for this reason, the agglutination of the binding system being decreased. It is to be noted 50 that it is possible to make use of other flame retarders as for example those based on antimony trioxide, bromine, potassium bromide, chlorine etc., in which respect, however, it is only the compounding formula used which gives such a good weight-to-effect relation. In this respect, migration of the additives, something likely to make the life of the filter shorter, is so small as to be unimportant.

- For producing the material of the present invention, in a first form of the process, a running length 60 of cotton fabric is run through a vacuum chamber (at 10 Torr), in which the running length is coated at separate points, using a roller and doctor system, with an adhesive composition at the rate of about 1000 points in each 10 cm². The cotton fabric is a 65 colored one, its degree of luster having undergone

adjustment as desired before hand, and having the desired level of IR remission.

- At once after coating of the running length of material, adsorber grains, more specially in ball-form, 70 that is to say spherical, are placed on the coated side at a distribution rate of about 4.5 million grains in each square meter. The grains may be put on by distribution through a screen, from which they are dropped onto the coated material, they then moving 75 to some depth into the inflated adhesive composition, becoming bonded to the adhesive compositions and, as the material is moved out of the vacuum space, being lifted upwards as the tops of columns, once the adhesive composition is forced 80 downwards on collapsing in the normal atmosphere. Hot-air drying then takes place and, next, corona-processing and ionization of the adsorber grains forming the top of the columns.

- In a further form of the process of the present invention, the adsorber grains undergo distribution 85 onto the adhesive composition using an electrostatic field. Then the support layer with the adhesive composition and the adsorber grains placed on it are run over a number of rollers causing a sudden change in the direction of motion so that the adsorber grains, 90 under the effect of centrifugal force, are moved away from and clear of the support layer, support columns of the adhesive composition being pulled out in the process by the adsorber grains. The speed, with which the support layer (half-completed product), 95 having the adhesive composition and the adsorber grains on it, is run over the guide rollers is about 400 m/min. Then further processing takes place as noted (drying, corona-processing).

- 100 In a third form of the process of the present invention for producing the material of the invention, the adsorber grains are mixed up with the adhesive composition and then the adhesive composition is placed on the support layer using a rail or doctor for producing an even layer. Next, this half-completed 105 product is moved over a slot nozzle producing air with an output (or throughput) rate of about 3000 cbm/min. Under the effect of the air moving upwards through the support layer, the adsorber grains are 110 lifted in an upward direction away from the support layer, pulling out, on doing so, adhesive material in the form of columns or hairs.

- The most useful form of the process for making the material of the invention is characterised in that 115 firstly again using the doctor and roller process as noted, the adhesive composition is run onto the support layer, for example in the form of cotton fabric, next, adsorber grains undergo distribution over the adhesive composition and then the half-completed product is turned through 180°, and then the half-completed product is turned through 180°, 120 and then, with the adhesive composition on top, it is moved through a hot air channel, in which, at 180°C the adhesive composition becomes so soft that the adsorber grains are moved downwards, under their own weight, pulling out hairs or columns of viscous adhesive composition, care being taken, naturally enough, to see that the adsorber grains are not 125 dropped off completely. Then the adhesive composition is caused to become solid so that stiff support

columns or hairs for the adsorber grains are produced. The turning round of the half-completed product to be facing downwards is, more specially undertaken by guiding using a roller. Later processing of the material at this stage is then undertaken as noted earlier.

The ionized material is preferably post-condensed on supports in autoclaves at about 120°C for about 3 hours and then, before being used, it is kept for 3 days in a clean atmosphere for pressure equalization of the adsorber grains. In this respect, a high rate of circulation of the filtered air from the atmosphere is very important.

The adsorber grains may be spherical, but, however, they may take on any other form, as for example in the form of pyramids, blocks, etc.

For this reason, in the case of the material of the invention, the adsorber grains are fixed on a support material or a support layer with the help of a gel able to be thermo-sealed (thermo-fixing). The adsorber grains preferably have a diameter of about 0.1 to 0.7 mm.

It has turned out that with the material of the present invention, the adsorption efficiency is better than that of the German Offenlegungsschrift specification 2,804,154, while keeping to the same weight for a given area. Furthermore, because there is no foam material support or base, the volume of the material of the present invention is about 50% lower than in that of the German Offenlegungsschrift specification 2,804,154.

Because use is not made of any polyurethane substance in or as the foam material support, hydrolysis is not possible. Furthermore, the rate of aging is very much less, that is to say the life of the material of the present invention is very much longer than that of the prior art material.

It has furthermore turned out that the material of the present invention is very pliable. The fire proofing properties behaviour in a fire are very much better because there is no chance of material melting and taking the form of falling drops under the effect of heat. Testing has made it clear that after the effect for about 16 seconds of a flame at 1200°C there is no lowering of the filtering properties of the material of the present invention.

Specially high-level properties are produced against the effect of chemical damaging substances, napalm or heat, if the material has a number of layers, for example seven layers. The first layer is, more specially, formed by a flame-proof, water and oil-repellent fabric, knitted material or a batt of mineral fibers. The second layer is a joining layer of plastics, while the third layer is again a fabric, knitted material or a batt, it having been processed by the first layer or being made of such materials that it becomes flame-proof and water- and oil-repellent. The fourth layer is made up of the adhesive composition as noted, that is to say hairs or columns of adhesive composition supporting the adsorber grains, which, on the columns, take the form of the fifth layer. The sixth layer is in the form of the hyperboloid joining bridges between the adsorber grains, while the seventh, and in the case of protective clothing, innermost layer, is the same as the first layer

in form.

This many-layer material was tested for 16 seconds using a free flame at a temperature of about 1000°C, it turning out that only the first, that is to say in the case of protective clothing, the outermost layer, was carbonized. The mechanical strength and adsorption properties of the fifth layer were kept in full.

CLAIMS

1. A material for protection against chemically damaging substances and short-term heating effects made up of an air-pearmeable flexible support layer for adsorber particles, more specially porous adsorber grains, characterised in that the adsorber grains are placed on support columns, present on at least one side of the support layer.

2. A material as claimed in claim 1, characterised in that the adsorber grains are round.

3. A material as claimed in claim 1 or claim 2, characterised in that the support layer is a fabric, more specially cotton material, and in that the support columns are in the form of an adhesive composition changed into a solid form.

4. A material as claimed in claim 3, characterised in that the adhesive composition is made up generally of:

polymer (in latex) 100 parts

zinc oxide 5 parts

sulfur one part

5. carbon black 3 parts

hard kaolin 10 parts

thiocarbamilide 1 part

zinc dibutyldithiocarbamate 2 parts.

5. A material as claimed in claim 3 or claim 4, characterised in that the adsorber grains are grafted or tacked on the support columns.

6. A material as claimed in anyone of claims 1 to 5, characterised in that the support layer is made of a material or impregnated in such a way that it is hardly flammable and is furthermore oil and water-repellent.

7. A material as claimed in anyone of claims 1 to 6, characterised in that it is made up of seven layers, that is to say a first layer in the form of a flame-resistant, water and oil-repellent fabric, knitted material or batt of mineral fibers, the second layer is a joining layer made of plastics, the third layer again takes the form of a fabric, knitted material or a batt of mineral fibers, the fourth layer is in the form of the adhesive composition with support columns, having the adsorber grains seated on them, the adsorber grains forming the fifth layer, the sixth layer is formed by hyperboloid adhesive bridges, joining up the adsorber grains, and the seventh layer is a covering layer of flame-resistant, water- and oil-repellent fabric, knitted material or batt of fibers.

8. A material as claimed in claim 7, characterised in that the adsorber grains are round and have a diameter of about 0.5 mm.

9. A material as claimed in claim 7 or claim 8, characterised in that the separate layers, in each case, are of such a size that, when acted upon by a flame with a temperature of about 1000°C for about 16 sec only the first layer is carbonized, with the outcome that the mechanical strength of the structure is

kept up to the necessary level by the third layer and the adsorbing properties are kept up at the desired level by the adsorber grains forming the fifth layer.

10. A material as claimed in anyone of claims 4 to 9, characterised by the adhesive composition's containing, as latices, chloroprenes, natural latices, acrylates, polyurethanes, silicone rubber, fluoroprenes, polyvinylidenes and compounds and/or mixtures of them.

11. A process for making a material as claimed in anyone of claims 1 to 10, using an air-permeable, flexible support layer for adsorber particles, more specially porous adsorber grains, characterised in that at separate points an adhesive composition, which at the start is viscous, is placed on the support layer, the adsorber grains are placed on the adhesive composition while still viscous and then this half-completed product is mechanically so processed that the adsorber grains have the effect of pulling up the adhesive composition to take the form of support columns so that the adhesive composition then takes on a solid form.

12. A process as claimed in claim 10, characterised in that the adsorber grains are positioned on the outer face of the adhesive composition, more specially with a distribution rate of about 4.5 million grains/sqm.

13. A process as claimed in claim 10 or claim 11, characterised in that the half-completed product is acted upon by a vacuum for forming the support columns.

14. A process as claimed in claim 10 or claim 11, characterised in that the half-completed product is moved over guiding rollers so that the adsorber grains, under the effect of the centrifugal forces produced, are responsible for pulling out the adhesive composition in the form of columns.

15. A process as claimed in claim 10, characterised firstly by the addition of adsorber grains to the adhesive composition, by the later distribution of the adhesive composition with its adsorber grains over the support layer by the use of a blade or the like, and by moving this half-completed product over an air nozzle in such a way that the outcoming air is forced through the support layer lifting the adsorber grains upwards away from the support layer with the forming of support columns.

16. A process as claimed in claim 15, characterised by the use of a slot nozzle with an air outlet rate of about 3000 m³/minute.

17. A process as claimed in claim 10 or claim 11, characterised in that the half-completed product is so turned that the support layer is on top, then the half-completed product is moved in this position through a hot air conditioning apparatus in which it is heated to a temperature at which the adhesive composition becomes so soft that the adsorber grains are moved downwards under their own weight for forming support columns and then the adhesive composition is changed into a solid condition.

18. A process as claimed in anyone of claims 10 to 17, characterised in that the support columns are ionized.

19. A process as claimed in claim 18, character-

ised in that the ionized material is post-condensed in an autoclave or the like at an increased temperature for a certain time.

20. A process as claimed in claim 11 substantially as described above.

21. A material as claimed in claim 1, substantially as described above or produced by the process as claimed in anyone of claims 11 to 20.

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